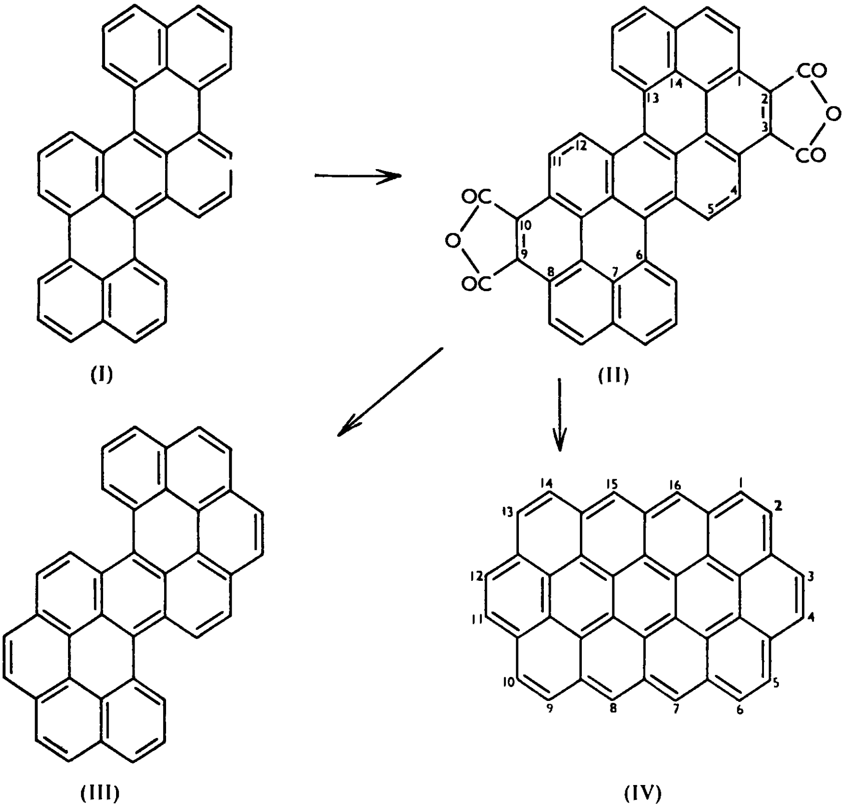
754. *Circumanthracene and Dinaphtho*(7′ : 1′-1 : 13)(1″ : 7″-6 : 8)-*peropyrene.*

By E. Clar, W. Kelly, J. Monteath Robertson, and M. G. Rossmann.

Di*peri*naphthyleneanthracene (I) was condensed doubly with maleic anhydride with the formation of the compound (II), which with copper powder and quinoline gave the hydrocarbon (III). Decarboxylation with soda-lime yielded the same hydrocarbon (III) and the more condensed product (IV), whose structure was proved by *X*-ray examination.

When di*peri*naphthyleneanthracene * (I) is melted with maleic anhydride one molecule of the latter is added endocyclically in the central anthracene complex.[1] This adduct dissociates into its components when heated above 200°. However, if the hydrocarbon (I) is boiled with maleic anhydride in presence of chloranil as dehydrogenating agent, two molecules are fused to it, with the formation of the tetracarboxylic dianhydride (II) in the same way as perylene reacts with one molecule of maleic anhydride.[2] The decarboxylation of this adduct with copper powder in boiling quinoline gives the orange-red dinaphthoperopyrene (III), whose absorption spectrum is reproduced in the Figure together with the spectrum of the starting material (I). The additional two benzene rings cause a strong violet-shift of the long-wavelength bands which is about twice the shift found in passage from perylene



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* The crystal structure of di*peri*naphthyleneanthracene has now been determined by *X*-ray analysis. This work will be published shortly.

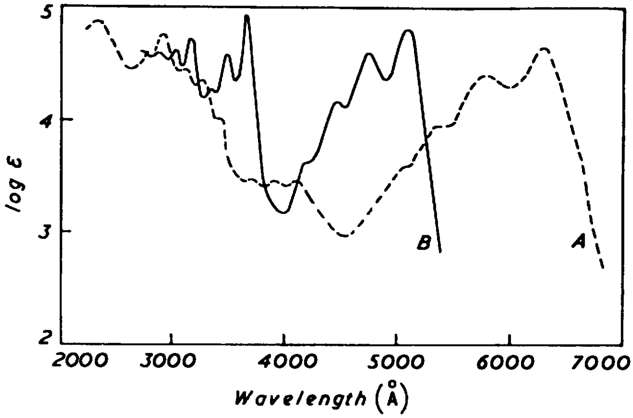
[1] Clar, Kelly, and Wright, *J.*, 1954, 1108.

[2] Clar, *Ber.*, 1932, **65**, 846.

to 1 : 12-benzoperylene. Treatment of the adduct with soda-lime at 400°, however, yields, besides the dinaphthoperopyrene (III), a higher-melting, less volatile hydrocarbon which sublimes in dark needles and gives a red solution in 1-methylnaphthalene.

The properties of this new hydrocarbon indicated that it might be formed by " controlled graphitisation " and might have the structure (IV), and this structure was proved by *X*-ray investigation which revealed the presence of the carbon atoms in the positions 8 and 16. This new hydrocarbon which is the third member of a series beginning with coronene and ovalene might be called " circumanthracene," because of the central anthracene complex which is completely surrounded by condensed benzene rings.

Measurement of the grey-black prismatic needles with copper $K\alpha$ radiation (λ 1·54 Å) showed that they are monoclinic with $a = 23{\cdot}77 \pm 0{\cdot}01$, $b = 4{\cdot}59 \pm 0{\cdot}03$, $c = 9{\cdot}98 \pm 0{\cdot}01$ Å, $\beta = 99° 54' \pm 30'$. The ($h0l$) spectra are absent when h is odd, and ($0k0$) when k is odd. The space group is therefore uniquely determined as $P2_1/a$ (C^5_{2h}). The volume of the unit cell is 1075 ± 6 Å^3. The density of the crystals, measured by flotation in potassium iodide solution, at 20° is $1{\cdot}52 \pm 0{\cdot}01$.



A, Absorption spectrum of 1 : 9-5 : 10-*di*peri*naphthyleneanthracene* (I). *Max.* (Å; log ε *in parentheses*) : 6300 (4·64), 5790 (4·40), 5360 (3·96); 4120 (3·47), 3920 (3·47), 3720 (3·47); 3420 (4·02), 3280 (4·36), 3120 (4·44), 2920 (4·76) *in benzene*; 2360 (4·88) *in alcohol.*

B, Absorption spectrum of dinaphtho(7′ : 1′-1 : 13)(1″ : 7″-6 : 8)*peropyrene* (III). *Max.*: 5100 (4·80), 4760 (4·59), 4470 (4·16); 3670 (4·92), 3490 (4·58), 3340 (4·26); 3170 (4·72), 3040 (4·61), 2900 (4·59) *in benzene.*

The space group $P2_1/a$ requires four asymmetric molecules or two centrosymmetric molecules per unit cell. If we assume two molecules, the above data give M 492 ± 5 (Calc. for $C_{40}H_{16}$: M, 496·5. Calc. for $C_{38}H_{18}$: M, 474·5).

The molecular weight is thus established with considerable accuracy, but much more detailed evidence regarding the structure of the molecule can be obtained by comparing the crystal data with those for coronene and ovalene (see Table). The b and c axes remain very constant for the three crystals, but there is a steady increase in a and decrease in β as we pass from coronene to circumanthracene. This is strong evidence that all these crystals are of the same structural type, a conclusion which is confirmed in detail by a study of the *X*-ray spectra.

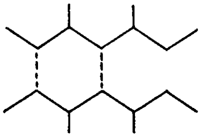
Crystal data.

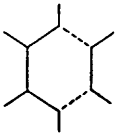
	a (Å)	b (Å)	c (Å)	β	Space group	Z	d	M
Coronene, $C_{24}H_{12}$	16·1	4·70	10·2	110·8°	$P2_1/a$	2	1·38	300
Ovalene, $C_{32}H_{14}$	19·5	4·70	10·1	105·0	$P2_1/a$	2	1·49	398
Circumanthracene, $C_{40}H_{16}$	23·8	4·59	10·0	99·9	$P2_1/a$	2	1·52	496

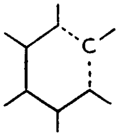
By setting up a trial structure based on the analogy with coronene and ovalene it was found that most of the ($h0l$) structure factors could be explained. A Fourier synthesis based on this trial structure yielded a very clear electron-density projection of the molecule, which showed all the carbon atoms in the positions expected from structure (IV). Further refinement is proceeding, but is difficult because of a rapid decrease in the intensities of the high-order reflections, which appears to be due to an unusually high temperature factor. At the present stage of refinement, however, the discrepancy between calculated and observed structure factors has been reduced to about 19%. At this point there can now be no reasonable doubt that the structural formula is correct.

The origin of the carbon atoms in the positions 8 and 16 is not yet clear. They might come from the carbonyl groups or from the breakdown of another part of the molecule of the adduct (II) during the treatment with soda lime at 400°. (The problem is being studied in this Department, by means of the ^{14}C isotope.) The gap-filling in formula (III) is an example of the least well-known mechanism of ring formation in the course of graphitisation and building up a condensed ring system.

The best-known mechanism is the frontal condensation of 3 + 3 carbon atoms of two polycyclic systems, as indicated in diagram (V). This takes place under the influence of heat or aluminium chloride. The second possibility (4 + 2 carbon atoms) is given in (VI). It constitutes a diene synthesis analogous to the condensation of perylene with maleic anhydride or the reaction (I) ⟶ (II). But it might also involve an aromatic double bond at a higher temperature. The third possibility (5 + 1 carbon atoms) (VII), which seems to have been reported for the first time in this paper, probably includes the formation of radicals or bivalent carbon compounds.


(V)


(VI)



(VII)

EXPERIMENTAL

M. p.s were taken in evacuated capillaries. Microanalyses are by Mr. J. M. L. Cameron and Miss M. W. Christie.

Dinaphtho(7′ : 1′-1 : 13)(1″ : 7″-6 : 8)*peropyrene*-2 : 3 : 9 : 10-*tetracarboxylic Dianhydride* (II).—Di*peri*naphthyleneanthracene (I) (2 g.) and maleic anhydride (25 g.) were heated under reflux for 15 min. Chloranil (7 g.) was added and the reaction continued for 2¼ hr. The colour changed from violet-red to reddish-brown and a solid was precipitated. Boiling xylene was added and the precipitate filtered off hot and washed with hot xylene. The dark purplish precipitate of the dianhydride (II) could not be successfully crystallised from any solvent. It was dissolved in ethanolic potassium hydroxide, and the solution diluted with water and acidified to give a dark purplish-red precipitate of the *tetracarboxylic acid* (Found : C, 76·4; H, 3·1. $C_{42}H_{18}O_8$ requires C, 77·5; H, 2·8%). The acid dissolved in warm concentrated sulphuric acid to a greenish-blue solution.

Dinaphtho(7′ : 1′-1 : 13)(1″ : 7″-6 : 8)*peropyrene* (III) *and Circumanthracene* (IV).—(a) *Decarboxylation with soda-lime.* The dianhydride (2·4 g.) and soda-lime (20 g.) were ground together to a smooth paste with a little alcohol. The mixture was heated at atmospheric pressure in a sublimation tube to remove moisture, and the pressure was slowly reduced. The mixture was heated at about 400°/1 mm. until no further material sublimed (about 12 hr.). The sublimate was extracted several times with boiling xylene. The crystals which separated from the combined extracts were filtered off and the xylene filtrate was concentrated and chromatographed on alumina with benzene as eluant. The orange-red eluate had a green fluorescence and yielded fine orange-red needles (0·1 g.), m. p. 338—339°, of *dinaphthoperopyrene* (III) (Found : C, 96·3; H, 3·8. $C_{38}H_{18}$ requires C, 96·2; H, 3·8%). It dissolved in warm concentrated sulphuric acid to a magenta solution.

The residue from the xylene extraction was crystallised from 1 : 2 : 4-trichlorobenzene, and the crystals were combined with those from the xylene extraction and chromatographed on alumina with trichlorobenzene as eluant. The first, reddish band yielded a small quantity of dinaphthoperopyrene. A second, reddish-purple band on elution gave a deep red solution from which were obtained long black needles of *circumanthracene* (IV) which sinter at 480° but do not melt clearly at higher temperatures (Found: C, 96·3, 96·5; H, 3·45, 3·6. $C_{40}H_{16}$ requires C, 96·75; H, 3·25%). It dissolved with an orange colour in concentrated sulphuric acid.

(b) *Decarboxylation with copper powder.* A small quantity of the dianhydride (II) was heated with some copper powder in quinoline for 2 hr. The quinoline solution was filtered into dilute hydrochloric acid, and the precipitate sublimed in a vacuum. The dark reddish sublimate contained no trace of circumanthracene and on purification was identical with the dinaphthoperopyrene obtained as above.

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